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THE EFFECT OF COMPOSITION ON THE M_s AND DECOMPOSITION TEMPERATURES IN STAINLESS STEELS

By

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ABSTRACT

The martensite reaction has been followed in simple 18-8 type stainless steel alloys by means of electrical resistivity. A linear equation has been determined using the method of least squares relating the alloy composition and the temperature at which martensite is first observed to form during cooling.

The decomposition of martensite at elevated temperatures has been investigated using electrical resistivity measurements; and the decomposition products have been examined metallographically.

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The formation of martensitic ferrite in stainless steels has a pronounced effect on the mechanical and corrosion properties of stainless steels. In addition, the decomposition of martensite at elevated temperatures has an important bearing on both the structure and the strength of an alloy at elevated temperatures[2].

Eichelman and Hull[1] determined graphically an equation relating the M_s temperature and the chromium, nickel, carbon, nitrogen, manganese and silicon contents on the basis of twenty-one alloys, using dilatometric measurements to detect the start of martensite formation. They conducted a thorough review of the literature and summarized the composition equivalents of the various elements to form ferrite from austenite.

EXPERIMENTAL PROCEDURE

The alloys for this program were prepared from ingot iron, electrolytic nickel, and low and high carbon ferro-chromium, and were deoxidized with a calcium-manganese-silicon alloy. Some of the alloys were melted in a thirty-pound induction furnace and cast in graphite molds. The ingots were forged to one-half inch diameter rods at a maximum temperature of 2200° F. The rods were solution treated one-half hour at 2000° F and oil quenched. Samples 3/16 inch in diameter by 1-1/2 inches long were machined from these rods for resistivity measurements. The balance of these alloys was used in other research programs to evaluate the effects of composition and structure on high temperature creep-rupture strength and are reported elsewhere[2,3,4].

The remaining alloys were melted in an indirect carbon arc furnace as approximately six-pound heats. Prior to casting in graphite molds,

rods for resistivity measurements were sucked up in Vycor tubes. These rods were successively cold swaged and homogenized at 2000° F in a helium atmosphere to break up the cast structure. The grain size was found to be fairly consistent, varying between ASTM 3 and 6.

The chemical compositions are listed in Table I and are presented graphically in Figure 1. Extreme care was taken to double or triple check all carbon and nitrogen analyses. The nitrogen values listed are wet analyses but were carefully checked by vacuum fusion analyses.

Resistivity measurements were made with a Kelvin double bridge which has an accuracy of 0.1 percent in the resistance range investigated. Stainless steel lead wires for the resistance measurements were spot welded to the specimen to minimize spurious voltages arising from thermal gradients. A chromel-alumel thermocouple was wired to the center of the resistivity specimen for the temperature measurements.

Each resistivity specimen was held 1/2 hour at 1850° F prior to starting the test to dissolve any martensite or carbides formed during the preparation of the sample. The specimen was rapidly cooled through the carbide precipitation range and resistivity measurements were made through the temperature range of approximately 600° F to -320° F. To insure a constant temperature across the specimen, it was inserted in an uninsulated close fitting tube and the temperature gradient checked in several of the tests with three thermocouples. Measurements below room temperature were obtained by inserting the specimen in a double walled Pyrex glass tube surrounded by liquid nitrogen. A cooling rate of about 15° F per minute was obtained in this manner.

To study the decomposition of martensite at high temperatures, a furnace was constructed which maintained a heating and cooling rate of

TABLE I

The Composition and the Measured and Calculated M_s Temperatures of the Alloys of this Investigation

Alloy No.	Composition (in percent) Cr	Ni	C+N	Si	Mn	M_s(° F)	Calculated M_s Equation 1	Equation 2
1	12.8	4.5	0.115	*	*	500	556	571
2	11.4	5.7	0.078	0.07	0.13	475	624	653
3	11.8	6.1	0.104			450	487	503
4	12.5	6.1	0.127			440	382	384
5	13.2	6.6	0.080	0.05	0.08	400	408	415
6	12.0	6.1	0.091			400	509	527
7	13.0	8.6	0.087			360	250	246
8	16.3	6.0	0.088			330	244	225
9	16.0	6.1	0.097			325	230	209
10	15.3	6.5	0.093			325	244	223
11	15.8	6.1	0.088	0.14	0.09	300	267	258
12	12.4	5.8	0.155	0.08	0.11	300	346	337
13	13.9	6.1	0.125			275	296	286
14	10.7	11.8	0.051			275	121	115
15	12.0	8.1	0.092			275	303	304
16	11.7	8.0	0.097			270	321	322
17	13.7	8.1	0.079			265	225	214
18	14.3	7.8	0.084			260	193	178
19	11.5	10.4	0.061			245	182	183
20	13.4	8.7	0.077			240	159	181
21	13.8	6.7	0.156			235	132	134
22	15.8	5.9	0.148			225	132	97
23	12.7	8.3	0.095			220	229	222
24	11.8	8.6	0.143			170	132	110
25	13.7	8.0	0.139			140	78	44
26	15.7	8.7	0.060			100	77	53
27	12.9	9.8	0.098			55	55	34
28	18.1	8.3	0.035			50	29	-1
29	11.7	11.1	0.072			35	71	37
30	18.1	5.9	0.139			0	0	-50

TABLE I (Continued)

Alloy No.	Composition (in percent) Cr	Ni	C+N	Si	Mn	Ms (°F)	Calculated M_s Equation 1	Equation 2
31	17.4	8.3	0.055	0.29	0.09	-25	22	-9
32	11.5	10.9	0.098			-40	35	14
33	13.7	9.3	0.068	0.06	0.13	-60	131	121
34	18.5	6.5	0.082			-60	74	19
35	12.9	8.7	0.112			-65	131	108
36	16.6	8.2	0.100	0.18		-75	-31	-72
37	16.2	9.3	0.066			-125	-32	-59
38	14.1	8.8	0.176			-125	-126	-185
39	13.9	9.6	0.120	0.11	0.08	-130	-50	-88
40	13.5	10.0	0.100			-135	-12	-40
41	18.3	8.2	0.074	0.21		-140	-78	-123
42	18.5	6.1	0.151		0.09	-150	-76	-141
43	13.3	12.2	0.070			-150	-144	-176
44	12.4	11.7	0.096			-175	-99	-135
45	18.4	8.2	0.114	0.19		-200	-188	-254
46	18.5	8.1	0.112		0.03	-200	-177	-242
47	15.4	12.0	0.070			-200	-257	-314
48	15.7	10.2	0.102			-210	-181	-234
49	17.2	8.2	0.151		0.09	-250	-205	-275
Sum of differences between measured and calculated M_s							3065° F	3229°F
Average difference between measured and calculated M_s							63° F	66°F

Not analyzed for Mn and Si

25° F per minute. Since the reversion temperature to austenite obtained with a heating rate of 25° F per minute is not the equilibrium reversion temperature, isothermal tests were also conducted at several temperatures in the decomposition range. In order to start with the same structure each time, especially where more than one test was performed, all specimens were first heated to 1850° F for one-half hour and then quenched to -320° F prior to testing for the martensite (ferrite) reversion temperature.

To study the effect of stress at temperature on the reversion of martensite, sub-standard tensile specimens (.160" diameter and 1.0 inch gage length) of alloy 31 were wired for resistivity measurements and stressed to produce plastic deformation in the temperature range of the martensite reversion.

Samples of several of the alloys were heated in a high temperature X-ray camera and diffraction patterns were made at various temperatures to identify the phases present and to correlate them with changes in resistance.

After testing, each sample was sectioned and examined metallographically to determine the phases present and to check the grain size.

Figure 2 shows the typical form of a heating and cooling curve for one of the alloys. The results of the high temperature X-ray diffraction studies are superimposed on this curve. The formation of martensite in these alloys can be seen to result in a sharp increase in resistivity during cooling. The decomposition and resolution of martensite (ferrite) during heating is accompanied by a decrease in resistance. The M_s temperature is defined as that temperature during cooling at which the initial increase in resistivity is first observed. The use of resistivity measurements permits quick, simple identification of the M_s temperature. The measured values of M_s for all of the alloys are presented in Table I. It

might/well be to point out that in order to minimize carbide and nitride precipitation, which cause an increase in the M_s temperature, the alloys were rapidly cooled from the homogenizing temperature, and only the resistivity curve from 600 to -320° F was obtained.

Several alloys had to be eliminated from this investigation because subsequent metallographic examination showed them to have severe segregation and to contain delta ferrite. The presence of this latter phase results in a lower chromium austenite of indeterminate composition[5], which would introduce a significant error.

A linear relationship between composition and M_s was assumed and the constants were determined using the method of least squares in a digital computor. The following equation was obtained:

$$M_s = 2160 - 66\ (\%Cr) - 102\ (\%\ Ni) - 2620\ (\%\ C+N) \qquad (1)$$

For the purpose of comparison, the equation determined by Eichelman and Hull[1] has been rewritten below in the form of equation (1) using an average value for the manganese and silicon contents, 0.08 and 0.13 percent, respectively.

$$M_s = 2277 - 75\ (\%Cr) - 110\ (\%Ni) - 3000\ (\%\ C+N) \qquad (2)$$

The M_s temperatures were calculated for all the alloys on the basis of equations (1) and (2) and are also listed in Table I. Similarly the calculated M_s temperatures for the alloys in Eichelman and Hull's work are listed in Table II along with the chemical compositions and measured M_s temperatures. The constants for Si and Mn as determined by Eichelman and Hull, 50 and 60, respectively, were assumed to be correct and used in the calculation of the M_s temperatures. In addition, the error between the calculated M_s temperatures and the measured temperature was calculated for each group of alloys and the results are summarized with the average errors in each of the tables.

TABLE II

The Compositions and Measured and Calculated M_s Temperatures of the Alloys of Eichelman and Hull's Investigation

Alloy No.	Composition (in percent) Cr	Ni	C+N	Si	Mn	Measured M_s (°F)	Calculated M_s Eq. 1	Eq. 2
6696	11.9	9.7	0.059	0.42	1.39	174	142	140
6940	12.33	10.04	0.096	0.45	1.28	32	-16	-35
6908	12.24	10.25	0.069	0.42	1.33	4	40	28
6909	12.26	10.30	0.077	0.40	1.46	-55	6	-10
6903	12.18	12.04	0.063	0.47	1.36	-170	-129	-150
6865	14.38	9.06	0.042	0.36	1.21	10	97	90
6866	14.63	10.60	0.034	0.37	1.21	-60	-56	-75
6697	16.8	6.1	0.075	0.49	1.33	150	142	121
6902	17.30	7.56	0.081	0.49	1.33	-60	-53	-95
6625	16.6	10.2	0.028	0.46	0.63	-50	-94	-138
6694	12.0	10.0	0.059	0.42	1.31	114	109	104
6695	12.0	10.0	0.143	0.39	1.28	-82	-108	-144
6699	16.8	6.1	0.073	0.48	1.32	132	148	128
6700	16.8	6.1	0.160	0.44	1.31	-78	-77	-42
6939	12.13	10.13	0.089	0.43	1.32	-18	7	-11
6904	12.35	10.15	0.059	0.44	3.20	-68	-45	-51
6905	12.21	10.11	0.066	0.50	5.03	-142	-168	-171
6941	10.28	12.15	0.075	1.01	1.36	-110	-73	-82
6906	10.46	12.00	0.063	1.42	1.42	-143	-60	-28
6942	10.24	12.05	0.066	1.96	1.39	-97	-84	-90
6907	10.46	12.11	0.048	2.58	1.37	-110	-87	-80
Sum of difference between measured and calculated M_s							652° F	779° F
Average difference between measured and calculated M_s							31° F	37° F

TABLE III

Alloy Composition, Measured M_s Temperatures, and Reversion Temperatures from Isothermal Tests

Alloy No.	Composition (in percent) Cr	Ni	C	N	M_s (°F)	Minimum Reversion Temperature (°F)
31	17.4	8.3	0.020	0.024	-25	1140
50	14.5	6.7	0.040	0.023	150	1200
14	10.7	11.3	0.024	0.025	275	1080

Complete heating and cooling curves were determined for alloys 14, 31, and 50, and isothermal resistivity tests were conducted to determine the equilibrium reversion temperatures. These three alloys were chosen because of the large variation in chemical content (Cr, 11 to 17 percent) (Ni, 7 to 12 percent) and M_s temperatures (-25 to 275° F). Figure 3 shows the high temperature resistivity results for alloy 31; in addition, the reversion temperatures obtained on this and alloys 14 and 50 are listed in Table III. The initial rate of decrease in resistance was approximated from the isothermal tests and plotted as a function of the inverse of absolute temperature. In this way an approximate activation energy of 10,000 calories per mole was obtained, but the experimental inaccuracies of the measurements were found to be quite large.

In an attempt to identify the decomposition products of martensite, careful metallographic studies were conducted on the samples from the isothermal tests.

Plastically deforming alloy 31, containing martensite, at temperatures just below the minimum reversion temperature tc austenite did not transform any additional martensite within the accuracy of the resistivity method.

DISCUSSION

From the summary at the bottom of Tables I and II it can be seen that the temperatures calculated on the basis of equation (1) are somewhat closer to the measured M_s values than those calculated on the basis of equation (2). There was found to be an average deviation of 63° F (equation 1) as compared to 66° F (equation 2) for the alloys of this investigation (Table I). For the alloys from Eichelman and Hull's investigation, Table II, the average error was 31° F, using equation (1) and 37° F, using equation (2).

There are several contributing reasons for the slightly improved values using equation (1).

(a) The large change in resistance accompanying martensite formation as compared to the relatively small volume change, using dilatometry, permits a more exact determination of the M_s temperature.

(b) A greater composition range was covered in this investigation and a better distribution of alloy compositions was achieved as can be seen in Figure 1.

(c) Equation (1) was determined from 49 M_s temperature measurements while equation (2) was based on 21 measurements.

(d) The method of least squares was employed to determine the coefficients of equation (1) while the coefficients for equation (2) were determined graphically from two dimensional plots. Using the former procedure the whole 49 measurements could be utilized in the determination of each coefficient while in the graphical procedure only a portion of the 21 measurements could be utilized.

In spite of the above reasons for greater accuracy of the data, the error between the calculated and the measured M_s temperatures for the alloys in this investigation was found to be almost twice as large as the error for the alloys in Eichelman and Hull's work, regardless which equation was used to calculate the M_s temperature. It is improbable that this large difference can be attributed to a larger experimental error. In fact, just the opposite was expected based on the reasons listed above and coupled with the realization that great care was necessary in chemical analysis.

This leads one to question the assumption of linearity between M_s and composition. In using equations (1) and (2), it is assumed that the

effect of each element on the M_s is linear and does not vary with the concentration of the element. It is further assumed that the effect of each element is additive and independent of the effects of the other elements. Both assumptions are, of course, open to question. In fact, Cohen[6] and Zener[7], on the basis of free energy calculation, have each shown the M_s temperature to vary non-linearly as a function of carbon content for carbon percentages less than 0.2.

In an attempt to evaluate the merit of the assumption of linearity, the data were analyzed mathematically using a more generalized equation. A square term and a cross product term were added for each independent variable which would take into account the non-linearity and the interaction of the individual elements. This resulted in an equation with ten coefficients which were determined by the method of least squares in a digital computor. However, the resulting equation was of the wrong order of magnitude, due most likely to an insufficient amount of data to determine the ten coefficients accurately.

Because of this failure it was necessary to resort to a graphical approach to the problem. Since there are four variables, M_s, percent chromium, percent nickel, and percent carbon plus nitrogen, and only three dimensions available for plotting, one of the independent variables was corrected to a base value. It was then possible to plot the measured M_s temperature as a function of two of the other values.

On the basis of these three dimensional plots, the assumption of linearity with respect to chromium and nickel was found to be fairly valid over the chemical range investigated, within experimental limits. That is, the coefficients of these two elements were seen to be reasonably constant

and independent of each other and of the carbon plus nitrogen content.

On the other hand, the effect of carbon and nitrogen on the M_s temperature was found graphically to be non-linear and to depend in a fairly complex way on the chromium and nickel concentrations as well as on the carbon plus nitrogen concentration. The coefficient of carbon plus nitrogen was calculated using the chemical composition and the measured M_s temperature and is plotted against carbon plus nitrogen in Figure 4. The value obtained by the method of least squares in the digital computor, 2620, is marked on this plot. The variation is considerable but the variation is difficult to define correctly.

Since the assumption of linearity is not valid, the fit of a linear equation to experimental data should become increasingly inaccurate as the range, number, and distribution of the experimental data increase. This would then explain the greater error encountered in calculating the M_s temperatures of the alloys in this investigation as compared to the error for the alloys from Eichelman and Hull's[1] investigation.

The temperature for the reversion of martensite to austenite was determined accurately from isothermal resistivity tests for three alloys having a large variation in composition and M_s temperature. In general, the reversion of martensite was completed by 1200° F in all of the alloys in this investigation.

The metallographic studies of the decomposition products of martensite indicated that a general fine carbide precipitation took place in the areas of the old martensite platelets. The isothermal rate of decrease in resistance, which is roughly related to the rate of martensite decomposition, was measured as a function of temperature and gave an activation energy of

10,000 calories per mole. This is approximately the value of the activation energy for the diffusion of carbon. However, the experimental inaccuracies in the isothermal resistivity tests leave some doubt regarding the precision of this calculation.

The effect of stress at temperature on the martensite reversion also sheds some light on the decomposition reaction of the martensite. Since stresses resulting in plastic deformation were not found to cause any further measurable decomposition of martensite to austenite, it would appear that the reaction is not a reverse shear process in these alloys and therefore probably a diffusion controlled nucleation and growth reaction.

CONCLUSIONS

The martensite reaction was followed by resistivity measurements in a series of forty-nine stainless steel alloys to determine the effect of composition on the M_s temperature and on the decomposition of martensite at elevated temperatures.

The following linear equation was determined mathematically, which approximately relates the M_s temperature to the chemical composition:

$$M_s = 2160 - 66\ (\%Cr) - 102\ (\%\ Ni) - 2620\ (\%\ C+N)$$

The above equation is only approximate because the effect of C plus N on the M_s temperature is neither linear nor independent of the chromium and nickel compositions.

The reversion of martensite was found to be completed by approximately 1200° F for all the alloys. Metallographic and electrical resistivity results indicate that the martensite probably decomposes by a diffusion controlled reaction.

ACKNOWLEDGMENTS

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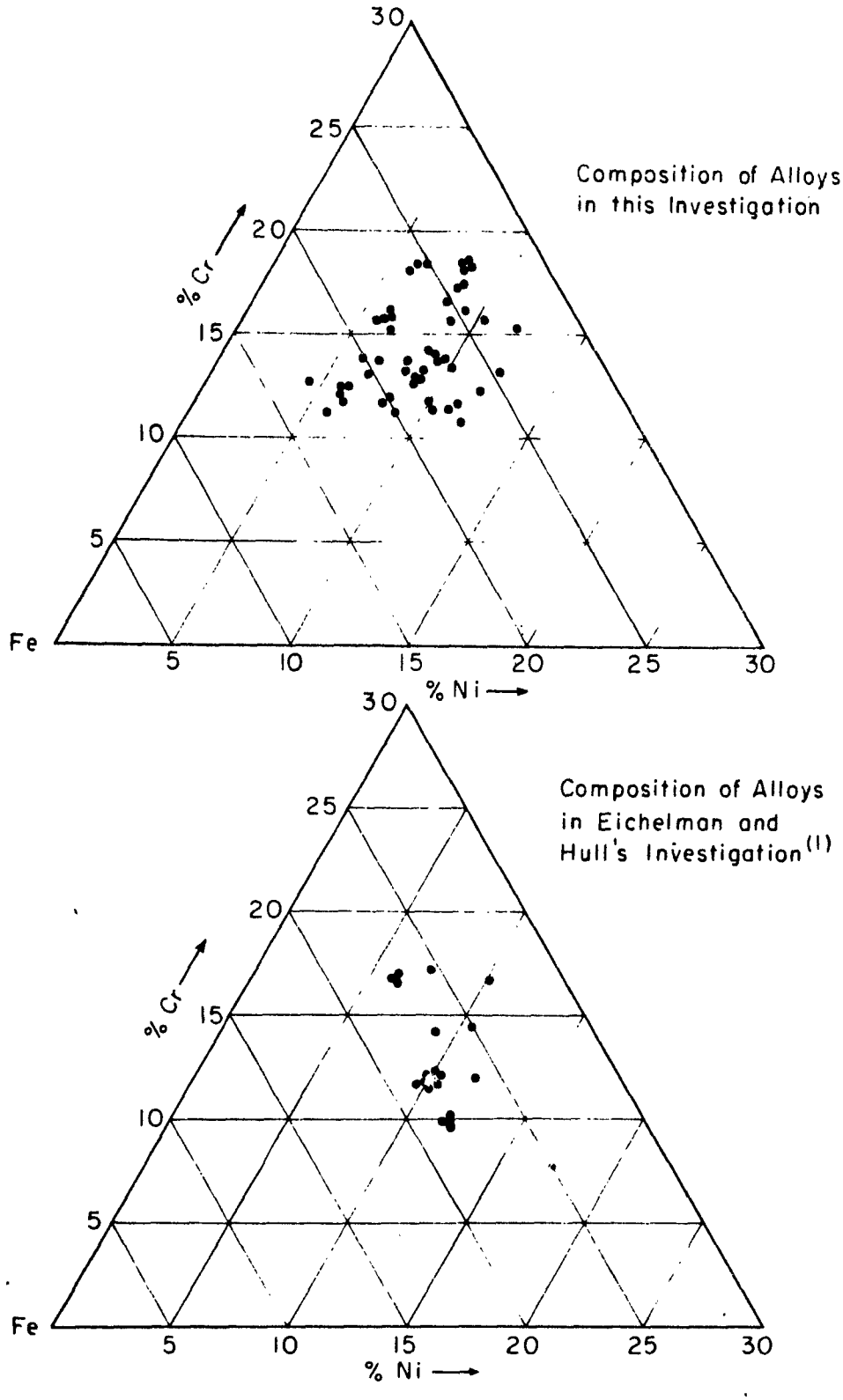

FIGURE 1 - GRAPHICAL REPRESENTATION OF ALLOY COMPOSITIONS OF THIS INVESTIGATION AND THAT OF EICHELMAN AND HULL[1]

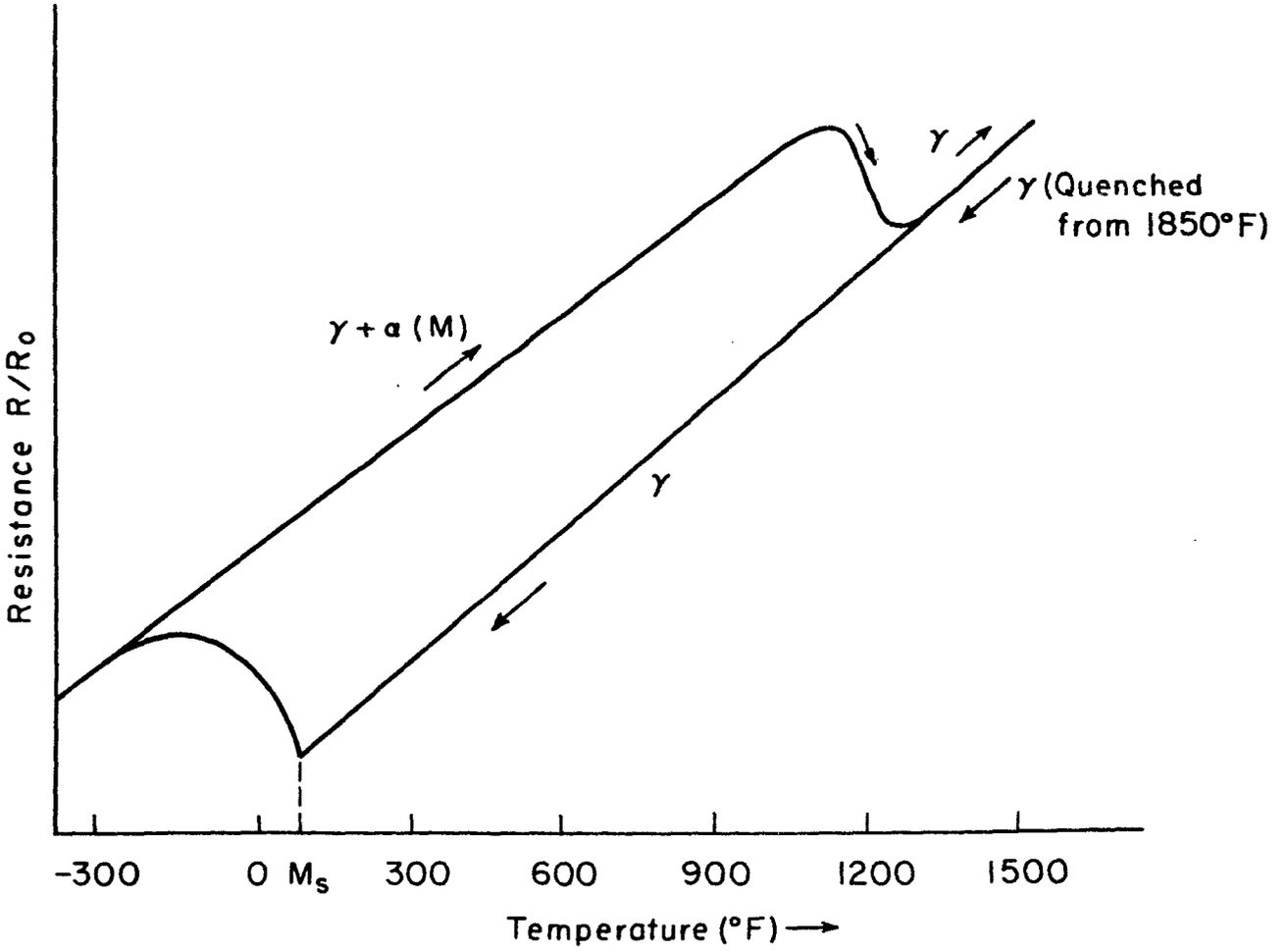

FIGURE 2-REPRESENTATIVE HEATING AND COOLING CURVE OBTAINED WITH RESISTIVITY MEASUREMENTS (SLIGHT AMOUNT OF CARBIDES MAY FORM AND PERSIST ON COOLING AND ON SUBSEQUENT REHEATING ABOVE ABOUT 1000°F).

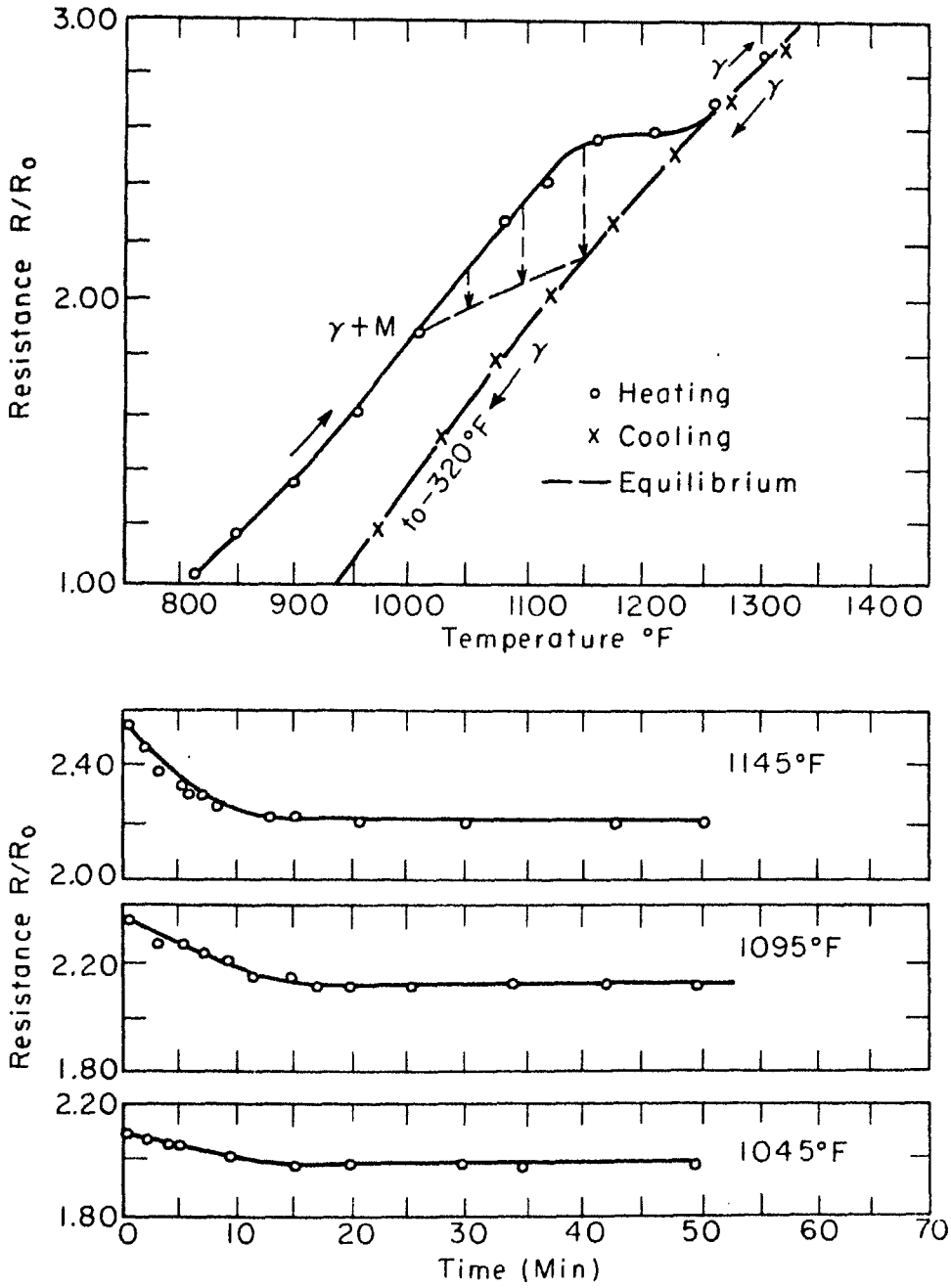

FIGURE 3 - RESISTANCE VS TEMPERATURE AND VS TIME FOR ALLOY 31 (17.4 % Cr, 8.3 % Ni, AND 0.044 % C + N) SHOWS RESISTANCE ON HEATING AND COOLING AT 25°F PER MIN. AND EQUILIBRIUM CURVE BASED ON ISOTHERMAL TESTS. SOME CARBIDES PRECIPITATE ON COOLING AND ON REHEATING IN 1000° TO 1500°F RANGE.

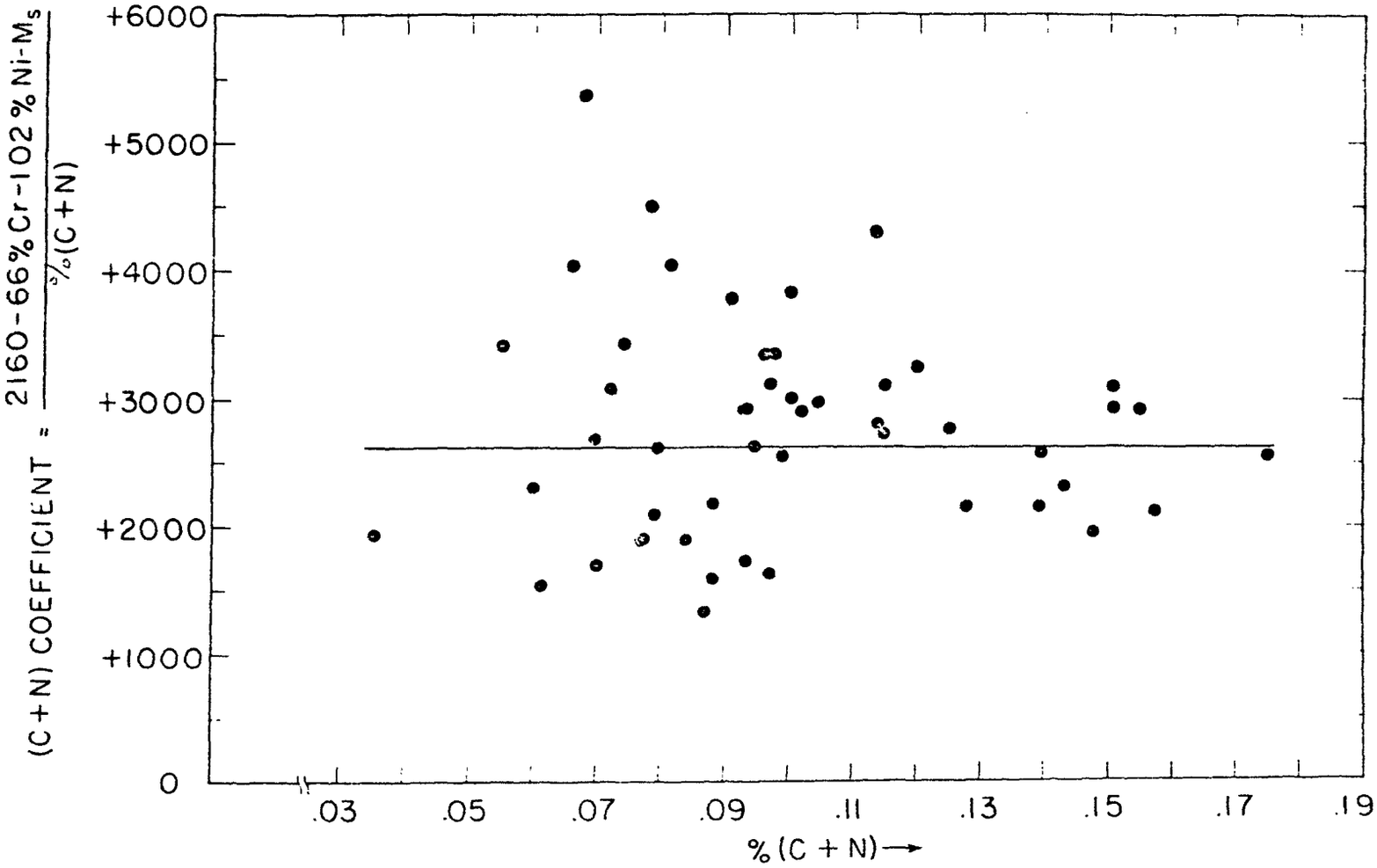

FIGURE 4 - PLOT OF THE CALCULATED COEFFICIENT FOR C PLUS N AS A FUNCTION OF C PLUS N.